



ANALYSIS OF THE COMBUSTION OF REFERENCE FUELS AS AN AID TO THE DEVELOPMENT OF A PERFECTLY STIRRED REACTOR FOR FUEL RESEARCH

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Abstract: *This work describes the use of simulations with detailed chemical kinetics as an aid in the dimensioning of a perfectly stirred reactor. This type of reactor is widely used in combustion studies due to its ability to promote rapid mixing and spatial homogeneity. The PSR is intended to be used for fuels research and its dimensioning depends on several considerations, like reactants consumption and sampling conditions. CHEMKIN-PRO™ was used to solve the equations for the combustion in a PSR, providing the relation between the inlet mass flow rate and the fuel decomposition at determined stoichiometry, temperature, and pressure. Simulations were conducted for five hydrocarbons from C1-C7. This data allows the adequate dimensioning of the PSR, flow meters and other laboratory instruments for a range of fuel and reactor conditions, likely to be found in the application. The simulations can also be used as references during commissioning tests to evaluate uncertainty sources.*

Keywords: *Perfectly stirred reactor, detailed chemical kinetics, fuel research, fuel surrogates.*

1. INTRODUCTION

Nowadays, one of the main trends in energy research is the study of environment-friendly fuels. These biofuels include alcohols obtained by biomass fermentation and esters derived from vegetable oils by transesterification. Their use is growing steadily due to its mixing, in amounts up to 20%, with conventional, petroleum-based fuels consumed in land transportation (Gail and Dagaut, 2007). The air transport sector is also compelled to mitigate its carbon footprint but the development of biofuels for aviation poses a greater problem, since the composition of kerosene is very constrained, given the extreme conditions under which combustion take place in a reliable and safe way (Blakey *et al.*, 2011).

In this context, detailed chemical kinetics combustion models of real fuels and potential surrogates are tools of great importance and their development heavily rely on well-established experiments like shock-tube, for the study of ignition delays, and perfectly stirred reactor, in which is possible to obtain mole fraction profiles of dozens species of interest as a function of temperature, stoichiometry, pressure and residence time. The perfectly stirred reactor (PSR) is an ideal chemical reactor of arbitrary form that neglects mixing limitations (Turns, 2011).

Currently, two of the most important PSR realizations are the well-stirred reactor (Longwell and Weiss, 1955; Manzello *et al.*, 2005) and the jet-stirred reactor (Dagaut *et al.*, 1986). Both realizations were developed based on concepts of heat and mass transfer in the mixing zone of turbulent jets and their quantitative data, both by using experimental approach, dates back to 1940s. The present work is part of an ongoing research project aiming at the development and testing of alternative fuel mixtures, including biofuels. Additional information, including the use of computational fluid dynamics to enhance the reactors geometry, is reported in other articles by the same authors.

2. PERFECTLY STIRRED REACTOR REALIZATIONS

As mentioned above, the perfectly stirred reactor (PSR), also known as continuously-stirred tank reactor (CSTR), is an ideal reactor of arbitrary form that neglects mixing limitations. In a system where either the mixing rates are high or

the chemical reaction rates are slow, the chemical kinetics constrains the reaction rates in the mixture and the residence time is the most important parameter of the reactor (Turns, 2011). Its physical realization considers a steady state flow of a known and homogeneous mixture of oxidant and fuel entering a reactor and being instantaneously mixed with combustion products, thus achieving uniform composition and temperature, while the combustion products are withdrawn from the reactor at the same mass flow rate. These conditions are so that outlet mass flow is identical in composition and temperature to the reactor contents.

Besides this general flow feature, a series of requirements are necessary to assure the usefulness of the experimental setup. In terms of versatility, the reactor must be capable of promote homogeneous mixture/reaction with variable residence time and pressure, thus a being able to produce intense stirring over a range of mass flow rate values. Additionally, the reactor must be made of an inert material, in order to avoid surface catalytic reactions, have minimum surface-to-volume ratio and total volume, to allow steady state operation, and be capable to conduct the kinetic process under controlled conditions, compelling its placement inside an electric oven or similar. The fulfillment of all these characteristics is unlikely and the experiment is necessarily a compromise among such complex constraints.

The basic concept of our PSR is based on that of Dagaut *et al.* (1986), which is an enhancement of the design proposed by Matras and Villermaux (1973). This realization is usually referred to as jet-stirred reactor (JSR), presented in Figure 1(a), in which the promotion of homogeneous mixing between reactants and products is effected by jets issuing from four injectors located in the equatorial plane of a spherical reactor. Figure 1(b) presents the new configuration developed in the present work.

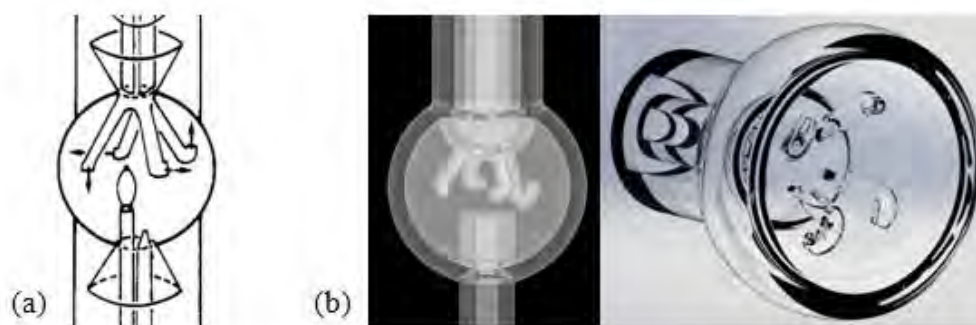


Figure 1. (a) Schematic of jet-stirred reactor by Dagaut *et al.*, 1986. (b) Enhanced configuration developed in the present work.

In spite of its ability to promote an adequate stirring of reactants and products, this geometry poses serious manufacturing issues. The balance between delicate geometric features and inert material compels the use of a fused silica (quartz) reactor, with the angles and diameters of the four curved injectors being critical. More details on the reactors design can be found in another article by the same authors in these proceedings, where CFD computations are employed to study the geometry of the four curved injectors and its effect on mixing and residence time.

To obtain nearly isothermal and homogeneous combustion the experiment should be carried out under a high degree of dilution on nitrogen or another inert gas, with fuel concentrations peaking 5000 ppm, resulting in a temperature increase below 30 K (Metcalf et al., 2009). This temperature rise could be negligible in very lean or very rich runs, since the reactor was designed to operate with equivalence ratios (the actual ratio of fuel and oxidant divided by the stoichiometric ratio of fuel and oxidant) ranging from 0.3 to 4.0. Pressure is also an important constraint, considering the aim of burning gaseous and liquid fuels, sometimes in conditions resembling those in gas turbine combustors. Another remarkable feature of this realization results from the design of the four injectors, allowing the probing in different positions to ensure that homogeneous mixing is achieved.

Some of these limitations of the PSR realization could be assessed with the use of detailed chemical kinetics mechanisms, developed using data from several different experiments, like shock-tube, rapid compression machine and the perfectly stirred reactor itself. The methodology employed in this assessment is described in the following section.

3. METHODOLOGY

As mentioned above, two of the most important PSR realizations for fuel oxidation studies present little quantitative data, if any, to rely on. Matras and Villermaux's JSR employed experimental data obtained by Hinze and Zijnen (1949) regarding the heat and mass transfer in a symmetrical jet issuing from a round orifice into quiescent ambient air, while Longwell and Weiss (1955) only refers to their design as a product of two year development. The extensive use of these experiments and the importance of the data obtained with them are remarkable but the availability of computational tools like both detailed chemical kinetics and CFD simulations provides a great framework for the study and

enhancement of these designs. In this work the use of CHEMKIN-PRO™ (2008) for reactor dimensioning will be presented.

The software CHEMKIN-PRO™ provides extensive mathematical modeling of several important reactor models employed in industrial processes, allowing the use of detailed reaction mechanisms in its simulations. For the perfectly stirred reactor, the hypothesis of perfect mixing means that the mathematical model has no dependence on flow parameters, hence there is no conservation of momentum. Also, with steady-state operation, the mass, energy and species balance equations are time independent, resulting in a model composed by a set of nonlinear algebraic equations instead of a system of nonlinear partial differential equations, and its solution is possible using a Newton-Raphson solver (Fogler, 2005).

The CHEMKIN-PRO™ simulations were carried out aiming to assess the dimensioning of the reactor itself and its accessory equipment like mass flow meters and gas chromatography/mass spectrometry systems. The main constraint in this problem is related to the JSR volume because the fused silica reactor is handcrafted from commercially available quartz piping and its effective volume is difficult to measure. A mockup, manufactured by a local glassware supplier, provided an estimative of attainable reactor volume of 44 ± 2 cm³.

The simulations were performed employing the PSR volume estimative and reaction mechanisms presented in the following subsection to solve a “Fix Gas Temperature” problem, as the ideal steady-state operation of the facility should occur. The simulation inputs are: reactor’s volume, temperature and pressure; reaction mechanism; problem type; fuel and oxidant composition and mass flow rates. The outputs are mean residence time and species concentration, from which fuel conversion is calculated. The reactor dimensioning is performed analyzing which values of mass flow rate result in attainable species sampling and reactants supply. Additionally, is possible to assess, for each fuel, which test parameters provide the conditions required to identify uncertainty sources.

3.1 Reaction mechanisms

For methane studies the reaction mechanism employed was NUI C5_49 (Healy *et al.*, 2010), which comprises 1588 elementary reactions involving 293 species. This mechanism was built based on shock-tube and rapid compression machine experiments with a quinary natural gas mixture [$\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8/n\text{-C}_4\text{H}_{10}/n\text{-C}_5\text{H}_{12}$] in the temperature range 630-1550 K, in the pressure range 8-30 bar and at equivalence ratios of 0.5, 1.0 and 2.0. One of the quinary mixtures tested had a methane concentration of 0.62, so the amount of larger hydrocarbon species was similar to those of nontraditional fuel sources like coal-derived natural gas. The ignition delay times studied with these mixtures are important tools for the design and efficient operation of gas turbines.

The simulations with acetylene were performed using Konnov 0.4 mechanism (Konnov, 1998), which accounts for 1027 reactions and 122 species. This mechanism was extensively validated against experiments including ignition delay times, species profiles on premixed laminar flames, species and temperature profiles on plug flow reactor and laminar flame speed, even though most of these validations were focused on H_2 , CO and syngas kinetics. The USC/Hai Wang mechanism (Qin *et al.*, 2000) was used for propane simulations. This detailed reaction mechanism comprises 463 elementary reactions involving 70 species and was built via computational optimization, based on the GRI-Mech 2.11, through the removal of nitrogen and propane chemistry and addition of a 258-reaction C_3 mechanism. While the mechanism focus on propane combustion, the parameter optimization targets included laminar flame speed and ignition delay times of CH_4 , C_2H_4 , C_2H_6 , C_3H_4 and C_3H_6 .

For isobutane studies the NUI C4_47 mechanism (Donato *et al.*, 2010) was employed, which accounts for 1319 elementary reactions involving 226 species. This mechanism was developed using ignition delay time data from shock-tube tests of n-butane and isobutane mixtures in the temperature range 1056-1598 K, in the pressure range 1-21 atm and at equivalence ratios of 0.3 to 2.0. These butane blends are of interest to gas turbine applications and the data obtained shows that 50/50 blend is more readily ignitable than pure isobutane but its reactivity is smaller than that of pure n-butane only in richer mixtures.

The simulations with toluene were performed using Andrae mechanism (Andrae *et al.*, 2007), which comprises 4635 reactions involving 1083 species. This mechanism is based on the Lawrence Livermore Combustion Group’s Primary Reference Fuel mechanism with the addition of a toluene sub-mechanism developed using shock-tube ignition delay time data. The Andrae mechanism was validated against shock-tube data for a mixture of 35% n-heptane and 65% toluene and for a gasoline surrogates consisting of 63-69% iso-octane, 14-20% toluene and 17% n-heptane. These tests were carried out in conditions relevant to HCCI combustion e.g., temperature 1200-1500 K and pressure 25-610 bar.

4. RESULTS AND DISCUSSION

For each fuel, a series of simulations assessed the hydrocarbon conversion as function of reactor temperature and mass flow rate, hence residence time, with pressure and equivalence ratio constrained to 1 bar and stoichiometric condition without dilution. The oxidant considered is air as a 79/21 volumetric mixture of molecular nitrogen and oxygen, so the continuous operation of the experiment will be limited by the nitrogen supply. A back-of-the-envelope

estimative of continuous test time, for a mean residence time of 100 milliseconds and using a nine cubic meter gas bottle, is around ~fifteen hours.

The simulations were carried out setting 0.1 SLPM as mixture flow rate and different temperatures to the reactor, in order to find the lowest temperature in which thermal ignition occurred. Following that, reactor temperature was raised in steps of 50 K and the mixture flow rate was ranged until residence time around 100 milliseconds or fuel conversion below 10% were obtained. From the point of view of commissioning test, it is important to know the test conditions more easily discernible from one another to assess which uncertainty source is critical. In the following results, these conditions are pointed out.

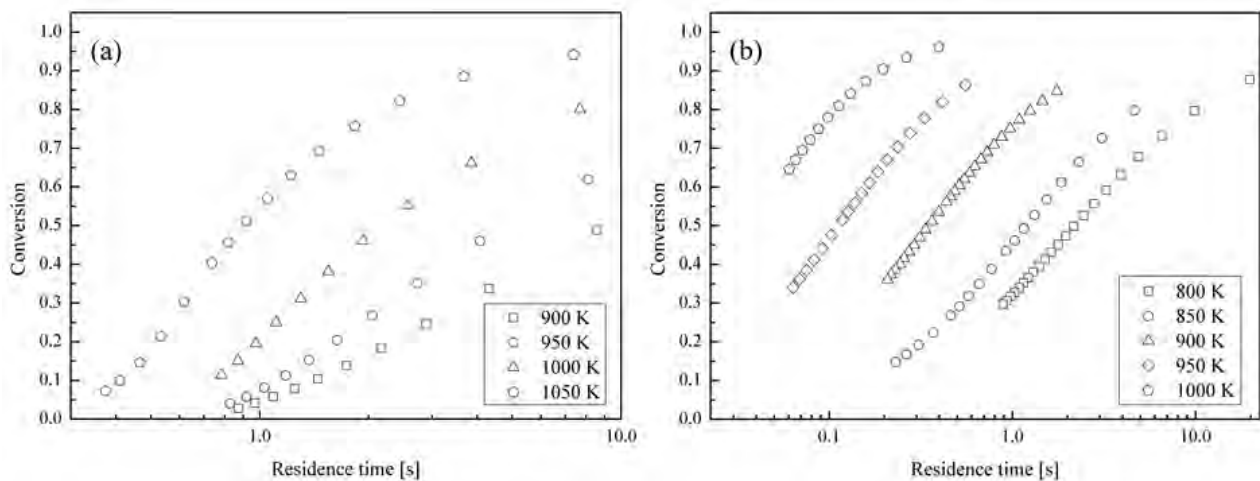


Figure 2. Fuel conversion as function of residence time and temperature for methane (a) and acetylene (b)

Figure 2 presents the results for pure methane and pure acetylene oxidation in a PSR. In the Figure 2(a) is clear that, for low mass flow rates, hence high residence time, a temperature increase from 900 to 1000 K results in a twofold increase in methane conversion. Since the mean residence time is calculated as a function of mixture density, it is possible to notice the reduction in residence time, for the same mass flow rate (0.1 SLPM), as a function of temperature, in the four rightmost points. Using these points it will be possible, for example, to evaluate that adequate mixing is achieved with low mass flow rate. Another interesting feature in Figure 2(a) is the increase in fuel conversion, following a temperature rise from 1000 to 1050 K, for residence time around one second.

For acetylene, Figure 2(b) highlights the high reactivity of this fuel, since a temperature increase from 800 to 1000 K results in a two orders of magnitude reduction in residence time to obtain similar fuel conversion. The 800 and 850 K points are very interesting from the point of view of commissioning tests because it will be possible to explore a wide range of conversion (0.3 to 0.8) with reduced reactants consumption (0.1 to 2.0 SLPM). The difference in fuel conversion between 850, 900 and 950 K, for a residence time of 0.3 seconds, is also useful to study the uncertainty sources of the facility, like mass flow meter and/or temperature sensor accuracies.

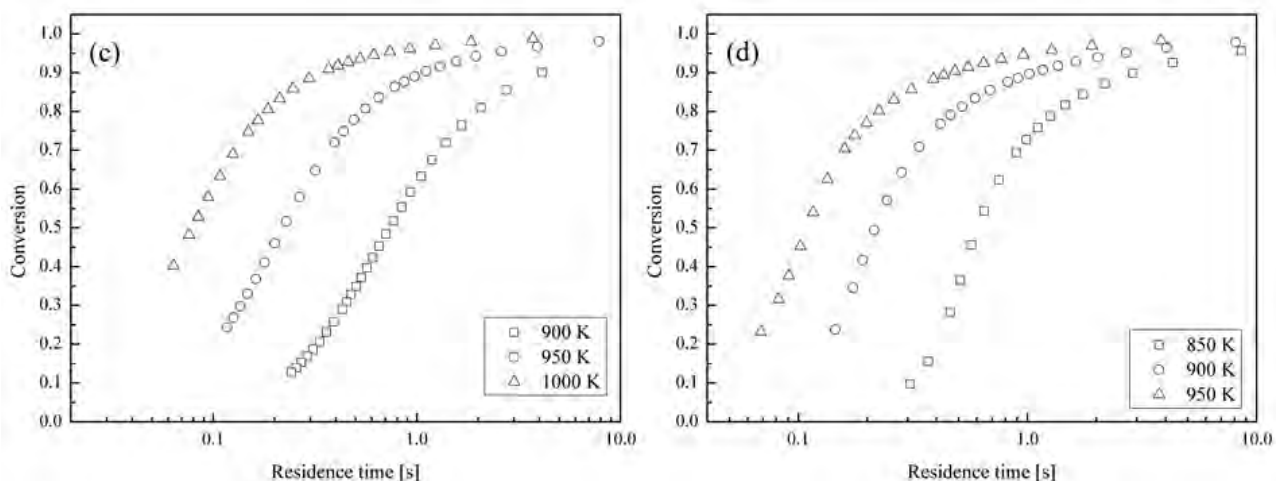


Figure 3. Fuel conversion as function of residence time and temperature for propane (c) and isobutane (d)

Figure 3(c) shows the results for pure propane oxidation. This fuel is also interesting for commissioning tests, as a temperature rise from 900 to 950 K results in a great change in fuel conversion, for residence times around 0.4 seconds. Other interesting test conditions are those around a 0.7 fuel conversion. It is also evident the asymptotic behavior of the fuel conversion for low mass flow rates, which was not so clear, within the experiment range, for the lighter hydrocarbons previously analyzed. For the isobutane oxidation, Figure 2(d), the interesting range of study is around a conversion of 0.5, where the influence of three temperatures could be better studied, as well as the conditions associated with the residence time around 0.3 seconds.

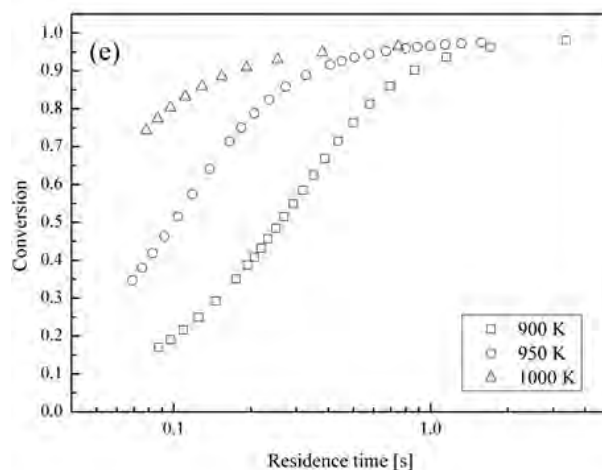


Figure 4. Fuel conversion as function of residence time and temperature for toluene (e)

Figure 4 presents the simulation results for toluene. This is an interesting fuel to study because it is a single-ring aromatic compound, as some components of jet fuel surrogates, and reaction mechanisms for it are available, even though these mechanisms lack extensive validation (Colket *et al.*, 2007). The results show an interesting range of study between 0.1 and 0.3 seconds, in conditions of high mass flow rate. Since the main objective of the project is the study of fuels heavier than toluene, this result suggests that tests with these fuels should be conducted with residence times below 0.1 second, resulting in very high nitrogen consumption, above 10 SLPM. The most likely solution is the use of a smaller reactor, to obtain lower residence times with lower mass flow rates. Since the reactor is handcrafted, is no easy task to achieve the adequate geometrical features, especially the injector's array, in a volume smaller than 40 cm³.

The simulation results obtained for the five fuels studied indicate that, in terms of experiment operation, the reactor's volume is a critical parameter regarding reactants consumption, but does not greatly affects the setup's ability to test light, gaseous hydrocarbons in stoichiometric conditions. However, tests with toluene and other single-ring aromatic compounds, which are of interest, are at stake since the favorable range of residence time to obtain characteristic fuel conversions is below 0.1 second, making this tests very demanding in terms of nitrogen consumption.

5. CONCLUSIONS

The perfectly stirred reactor is widely used in combustion studies due to its ability to promote rapid mixing and spatial homogeneity. In the last century, several realizations of this idealized reactor were developed, based on concepts of heat and mass transfer in the mixing zone of turbulent jets but the quantitative data was scarce. This work presents the use of detailed chemical kinetics as a project tool for the dimensioning of perfectly stirred reactor currently being developed at UFSC. The CHEMKIN-PRO™ software was employed to simulate the operation of PSR with five different hydrocarbon fuels, in order to evaluate the reactants consumption, the dimensioning of accessory equipment and test conditions that allow the study of uncertainty sources in the facility.

The results, presenting fuel conversion as a function of temperature and residence time, allow the identification of the favorable ranges of residence time where it is possible to assess the uncertainties related to mass flow accuracy and temperature accuracy, for example. For methane, these test conditions are around a residence time of 10 seconds, while for the other gaseous fuels analyzed, e.g., acetylene, propane and isobutane, these conditions occur between 0.1 and 0.5 seconds. For toluene the favorable residence time range is below 0.1 seconds, which is a difficult condition to achieve and sustain with the current estimative of attainable reactor volume because complies a high consumption of nitrogen, above 10 SLPM.

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Thereby, the results provided a range of mass flow rates expected to the reactants, essential to the specification of accessory equipment as well as an indicative of the current project limitations that should be dealt with in order to perform tests with liquid fuels like toluene and other single-ring aromatic compounds.

6. ACKNOWLEDGEMENTS

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